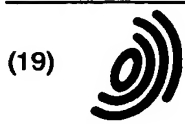


=US-A 5,316,696



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



4

(11)

EP 0 455 415 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
14.06.2000 Bulletin 2000/24

(51) Int. Cl.⁷: **C23F 11/12, C09D 5/08**

(21) Application number: **91303718.0**

(22) Date of filing: **24.04.1991**

(54) Anticorrosive composition

Antikorrosive Zusammensetzung
Composition anticorrosive

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **30.04.1990 GB 9009625**

(43) Date of publication of application:
06.11.1991 Bulletin 1991/45

(73) Proprietor:
IMPERIAL CHEMICAL INDUSTRIES PLC
London SW1P 3JF (GB)

(72) Inventor: Tury, Bernard
Prestwich, Manchester M25 8SE (GB)

(74) Representative:
Roberts, Jonathan Winstanley et al
Intellectual Property Department
ICI Chemicals & Polymers Ltd
P.O. Box 11
The Heath
Runcorn Cheshire WA7 4QE (GB)

(56) References cited:
• **DATABASE WPIL, NO. 81-74 846 DERWENT**
PUBLICATIONS LTD., London, GB & JP-A-56 109
261 (NSMO) 29-08-81
• **DATABASE WPI, NO. 78-75 466 DERWENT**
PUBLICATIONS LTD., London, GB & JP-A-53 105
534 (KAPA) 13-09-78

Poly oxy alkyl am
PIB Derivat
Hydroxyoxim.

EP 0 455 415 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to a new composition and is particularly concerned with a composition which is effective to improve the resistance of a metal to oxidative, and/or other, deterioration.

[0002] Metal surfaces which are exposed to weather are particularly vulnerable to oxidative deterioration and require protection. Oxidative deterioration of a metal may be reduced by contacting the metal with a suitable composition particularly a composition which has corrosion inhibiting properties.

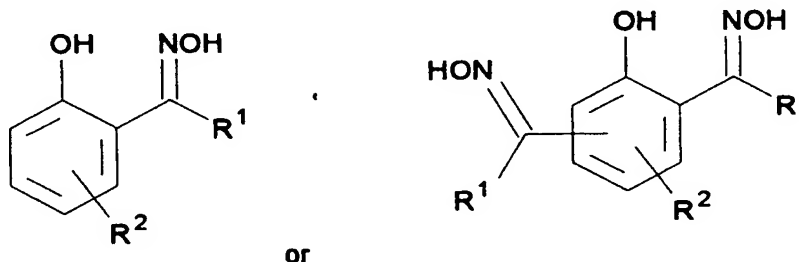
[0003] Compositions which can be used to reduce corrosion can be based on lubricants such as oils and greases. Such compositions contain at least one additive which is effective in retarding corrosion of a metal in contact with the lubricant. A wide range of materials have been proposed as additives to provide corrosion inhibition. Some of these materials contain lead or hexavalent chromium but there is a growing awareness of the toxicity of lead and hexavalent chromium and this has already resulted in some replacement of these materials by alternative materials. Slightly soluble metal salts of organic acids have been used as corrosion inhibiting additives in aqueous reservoir systems. Materials which have been proposed as corrosion inhibitors in metal coating compositions such as paint formulations, particularly for ferrous metals, include magnesium azelate (GB 1555468), zinc and lead 5-nitroisophthalates (GB 1531093), zinc cyanurate (US 4329381) and zinc and lead N-phenylglycinate (DE 3306064). Barium salts of hydroxy carboxylic acids such as salicylic acid have also been proposed (US 4304707). The salts of a divalent metal and a hydroxycarboxylic acid containing a fused ring system have also been disclosed as having corrosion inhibiting properties (EP 289155). Many of the foregoing metal salts are indicated to be very effective, and also to be useful in improving the performance of zinc phosphate when present at low levels. However, many of these materials have been mainly used in paint formulations.

[0004] In addition to the various metal salts which can be used as corrosion inhibitors, there have also been proposals to use organic compounds as corrosion inhibitors. Organic compounds proposed for use as corrosion inhibitors include oximes such as benzaldoxime (GB 1365291), salicylaldoxime, 2-hydroxy-5-alkylbenzaldoximes in which the alkyl group contains 7 to 13 carbon atoms (EP 125025), bis-oximes (EP 178850) and hydroxy oxime metal complexes (EP 206716), di- and tri-hydroxybenzene derivatives (GB 676632, GB 1045118, US 2429905 and EP 239288), alkenyl or alkyl succinic acid or anhydride and derivatives thereof (GB 1055337 and US 4326987) and polyesters and functionally terminated derivatives thereof (US 3415766, US 3574566 and EP 277711). Other corrosion inhibitors include, inter alia, organic acids and the esters thereof, primary, secondary and tertiary aliphatic amines and the amine and alkanolamine salts of organic acids, phosphorus-containing compounds and sulphur-containing compounds.

[0005] Various of the materials disclosed as providing corrosion inhibiting properties can be used in organic media, particularly oils and greases. However, not all materials which provide corrosion inhibiting properties can be used in oils or greases. Furthermore, we have found that different oils and greases respond in a different manner to the presence of a particular corrosion inhibiting additive. In particular we have found that a wide range of corrosion inhibiting additives have little effect when used in poly(oxyalkylene) glycol derivatives such as those used as lubricants. We have now obtained a composition based on a poly(oxyalkylene) glycol derivative and which has surprisingly useful corrosion inhibiting properties.

[0006] The present invention accordingly provides a composition comprising

- a) a liquid poly(oxyalkylene) glycol derivative,
- b) a carboxylic acid anhydride having a long saturated or unsaturated hydrocarbon chain which contains at least 6 carbon atoms, and
- c) a hydroxyoxime of the general formula:



where

R1 is a hydrogen atom or a substituted or unsubstituted hydrocarbon group; and

R2 is a substituted or unsubstituted hydrocarbon group in which the hydrocarbon group contains from 5 to 22 carbon atoms.

[0007] The liquid poly(oxyalkylene) glycol derivative is particularly one which is suitable for use as a lubricant and is typically a polymeric material containing alkylene oxide repeating units. More specifically, the liquid poly(oxyalkylene) glycol derivative contains ethylene oxide or propylene oxide repeating units, or may contain both ethylene oxide and propylene oxide repeating units.

[0008] The poly(oxyalkylene) glycol derivative is typically a product obtained by the alkoxylation of a mono-, di- or poly-hydroxy compound, particularly an aliphatic hydroxy compound such as methanol, ethanol, propanol, butanol or higher alkanol, a diol such as ethylene glycol or a polyol such as glycerol or pentaerythritol. In such compounds there are one or more poly(oxyalkylene) glycol chains, one end of which is linked to the residue of the hydroxy compound through an ether linkage.

[0009] The poly(oxyalkylene) glycol derivative may be soluble or insoluble in water. Poly(oxyalkylene) glycol derivatives which are soluble in water are typically those in which the (oxyalkylene) groups are solely or predominantly (that is at least 50% by weight) oxyethylene groups. Poly(oxyalkylene) glycol derivatives which are insoluble in water are typically those in which the (oxyalkylene) groups are solely or predominantly oxypropylene groups.

[0010] The poly(oxyalkylene) glycol derivative is a material which is in the liquid state, at least at the temperature of use, and preferably at a temperature of 25°C. The poly(oxyalkylene) glycol derivative may be suitable for use as a lubricant, for example as a gear oil or as the basis of a grease. Alternatively, if the poly(oxyalkylene) glycol derivative is a high viscosity, water-soluble material, it may be used in hydraulic fluids. The molecular weight of the poly(oxyalkylene) glycol derivative may be such that the material has a viscosity, measured at 40°C using the procedure of ASTM Test Method D445, which is in the range of from 5 up to 500,000 cSt, and more preferably in the range from 10 up to 250,000 cSt.

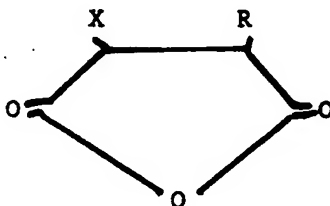
[0011] If the poly(oxyalkylene) glycol derivative is a water-insoluble material based solely or predominantly on oxypropylene repeat units, such a material typically has a viscosity in the range from 10 up to 1200 cSt.

[0012] If the poly(oxyalkylene) glycol derivative is a water-soluble material, based solely or predominantly on oxyethylene repeat units, such a material may have a viscosity in the range from 25 up to 250,000 cSt. If such a poly(oxyalkylene) glycol derivative is one which is suitable for use in oils or greases, it preferably has a viscosity in the range from 25 up to 1500 cSt. Water-soluble materials of high viscosity, that is having a viscosity in the range from 1500 up to 250,000 cSt and in general with a viscosity of at least 15000 cSt, are typically used in hydraulic fluids.

[0013] Suitable poly(oxyalkylene) glycol derivatives include, for example, water-insoluble materials which have a viscosity of at least 200 cSt up to 500 cSt. Suitable water-soluble materials have a viscosity of at least 100 cSt and preferably the viscosity does not exceed 750 cSt. Suitable poly(oxyalkylene) glycol derivatives are available as 'EMKAROX' (Registered Trade Mark) polyalkylene glycols from Imperial Chemical Industries PLC.

[0014] The long chain carboxylic acid anhydride (hereafter for convenience simply "anhydride") is preferably an anhydride of a dicarboxylic acid, particularly an α,β -dicarboxylic acid. The long chain which is present in the anhydride is a linear or branched, saturated or unsaturated aliphatic hydrocarbonyl radical and in particular is such a hydrocarbonyl radical which contains at least six carbon atoms.

[0015] As a preferred aspect of the present invention, the long chain carboxylic acid anhydride is a compound of the general formula (I),



wherein:

R is a long chain hydrocarbonyl radical which is linear or branched, saturated or unsaturated;

X is hydrogen or an alkyl, aryl, alkoxy or aralkyl group; or

R and/or X are linked to another cyclic anhydride group which may be the same or different; or

R and X together form a ring system which is substituted with at least one long chain hydrocarbonyl radical.

[0016] The anhydride is typically one in which X is hydrogen and R is a long chain hydrocarbonyl radical. By long

chain hydrocarbonyl radical is meant a hydrocarbon chain which contains at least six carbon atoms. The group R is especially a hydrocarbon chain which has a molecular weight of at least 100, whereby the group R typically contains at least 8 carbon atoms. The group R can be a linear or branched group such as nonyl, decyl, decenyl, dodecyl, dodecenyl, tetradecyl, tetradecenyl, hexadecyl, octadecyl, octadecenyl and the like and may be a mixture of different groups,

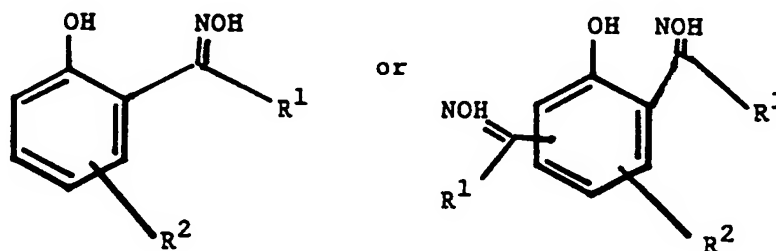
[0017] The group R can be derived from a polymeric material, for example an anhydride in which R is derived from an isobutylene polymer. Such anhydrides include succinic anhydrides (X is hydrogen in above formula) where the group R is an isobutylene polymer of molecular weight from about 200 to 8000, especially from 600 to 6000. It is particularly preferred in such derivatives that R is derived from an isobutylene polymer made from butene-1, butene-2 and isobutene. Materials of this type, which contain predominantly isobutylene units, are readily available and are referred to as polyisobutylene succinic anhydride, or PIBSA. Materials of this type are conveniently prepared by reacting the corresponding isobutylene polymer or a chlorination product thereof, with maleic anhydride.

[0018] If R and X together form a ring system, the resulting anhydride may, for example, be a long chain substituted derivative of phthalic anhydride in which the long chain substituent is as defined for the group R.

[0019] The corresponding acids derived from the anhydrides may be present in the long chain carboxylic acid anhydride and consequently the compositions in accordance with the present invention may also include these acids, which typically result from hydrolysis of the anhydride.

[0020] In addition to the anhydride, the composition of the present invention conveniently contains a further component which is a hydroxy-oxime.

[0021] The hydroxy-oxime included in the composition of this invention is a compound of the general formula:



where

R¹ is a hydrogen atom or a substituted or unsubstituted hydrocarbon group; and R² is a substituted or unsubstituted hydrocarbon group in which the hydrocarbon group contains from 5 to 22 carbon atoms.

[0022] The group R¹ is preferably a hydrogen atom but may be an alkyl, aryl or benzyl group, for example a methyl group. In the bis-oxime compound, the second oxime group is preferably in the 6-position and particularly preferred compounds of this type are the 2,6-bis(oximinomethyl)-4-alkylphenols such as 2,6-bis(oximinomethyl)-4-nonylphenol.

[0023] The group R² is preferably an alkyl group containing from 5 to 14 carbon atoms. The preferred mono-oximes are 2-hydroxy-5-alkylbenzaldoximes. The group R² may be a linear or branched, saturated or unsaturated group. Compounds in which R² is a branched alkyl group are particularly preferred. Suitable compounds of this type include 2-hydroxy-5-nonylbenzaldoxime and 2-hydroxy-5-dodecylbenzaldoxime. Compounds in which the group R¹ is a hydrocarbon group are the ketoximes such as, for example 2-hydroxy-5-nonylacetophenone oxime.

[0024] The weight ratio of the anhydride or mixture thereof with the corresponding acid, to the optional hydroxy-oxime may be between 99:1 to 1:99 but will generally be from 10:1 to 1:10, particularly from 5:1 to 1:5. However, the preferred proportions will be dependent on the particular compounds present in the mixture.

[0025] The composition of the invention may also include other materials, particularly materials which are known additives to lubricant compositions and particularly materials which can be used in poly(oxyalkylene) glycol lubricants. Such other additives include corrosion inhibiting materials such as, for example, petroleum sulphonates, aryl sulphonates and the metal salts thereof and other corrosion inhibiting materials of the types disclosed previously herein. Other additives which may be added to improve the properties of the composition include anti-oxidants, metal passivators, viscosity-index improvers, pour-point depressants, dispersants/detergents, anti-wear additives and extreme pressure additives. A wide range of materials suitable for such purposes are known. Anti-oxidants are typically phenols which may be monophenols or contain more than one phenolic group as in thio-bisphenols, alkylidene-bisphenols and the

esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with mono- or polyhydric alcohols such as octadecanol and pentaerythritol. Alternatively an amine antioxidant may be present. Metal passivators include triazoles and thiazoles and derivatives thereof such as substituted benzotriazoles and substituted 2-mercapto-benzothiazoles. Anti-wear additives include sulphur-and/or phosphorus-and/or halogen-containing compounds. The proportions of such other additives will be those known to the skilled worker in the lubricant field.

[0026] The other materials may be present in the composition in a substantial proportion of up to several times, for example up to ten times, by weight of the anhydride or the mixture of the anhydride, acid and/or the optional hydroxy-oxime. In general no particular advantage is achieved by using a large excess of the other materials and preferably the proportion of the other materials do not exceed twice the weight of the mixture and conveniently the other materials are present in essentially an equal proportion by weight relative to the weight of anhydride or the mixture thereof with acid and/or the optional hydroxy-oxime.

[0027] As noted previously herein, the compositions of the present invention provide improved corrosion inhibition. Certain compositions of the present invention also provide enhanced anti-wear properties and improved anti-oxidation properties.

[0028] Thus, as a further aspect of the present invention, there is provided a process which comprises contacting a metal with a composition in accordance with the present invention.

[0029] The process of the present invention is especially suitable for the corrosion inhibition of iron, zinc, copper, tin and aluminium and in particular mild steel and the zinc surface of galvanized steel.

[0030] The metal may be treated with the composition in any suitable manner and we have found it is useful to contact the metal with the composition and then to allow the composition to drain from the metal leaving a thin film, for example of thickness not more than 100 micrometres, of the composition on the surface of the metal to be protected. Alternatively, if it is being used as a lubricant such as a gear box oil, the composition is used in the conventional manner as a lubricant and at the same time provides the required protection against corrosion.

[0031] The proportion of the anhydride, or the mixture of anhydride and an acid and hydroxy-oxime, which is present in the composition is dependent on the manner in which the composition is to be used and will be greater under conditions in which a more severe corrosive environment is to be expected. In general the composition will contain at least 0.01% by weight, relative to the total composition of poly(oxyalkylene) glycol derivative anhydride, any corresponding acid and the hydroxy-oxime, of the anhydride or mixture of anhydride, corresponding acid and hydroxy-oxime and preferably will contain at least 0.1% by weight of the anhydride or mixture of anhydride, acid and hydroxy-oxime. For transport or storage, the composition can contain any suitable level of the anhydride, or mixture of anhydride, acid and hydroxy-oxime, for example up to 30% by weight or even higher. However, in use such high levels are generally not necessary in order to achieve a suitable level of protection against corrosion. Thus, the composition of the present invention typically does not contain more than 5% by weight of the anhydride or mixture of anhydride, acid and hydroxy-oxime and satisfactory corrosion inhibition has been obtained with compositions containing not more than 2% by weight of the anhydride or mixture of anhydride, acid and hydroxy-oxime.

[0032] The composition of the present invention may be used to provide temporary protection whilst a metal article is being transferred from one site to another. At the present time many metal articles are coated with a soft coating such as a grease or wax composition to provide protection whilst the metal article is being transferred. However, it is necessary to remove the soft coating composition from the metal surface prior to use. The composition of the present invention is more readily applied to the metal surface and subsequently removed. Furthermore, if the metal article is a part of an assembly of moving parts requiring lubrication, the composition may be used subsequently as the lubricant for the assembly of parts once this is in an operating condition. Thus, as an example, gear box castings may be coated with the composition of the present invention to provide temporary protection against corrosion whilst the castings are being transported and subsequently the gear box may be assembled without having to remove the composition from the metal surfaces, the assembled gear box subsequently being used either with a composition in accordance with the present invention as the lubricant or with a different lubricant with which the composition of the present invention is compatible.

[0033] The composition of the present invention provides a highly satisfactory protection against corrosion. However, a composition containing the liquid poly(oxyalkylene) glycol derivative and a hydroxy-oxime, in the absence of an anhydride, provides appreciably less protection against corrosion. The composition of the present invention provides protection against corrosion which is at least as good as that provided by the anhydride alone even though a lower level of anhydride is present in the composition containing the mixture.

[0034] Various aspects of the present invention are set out in the following illustrative examples in which all parts and percentages are by weight unless otherwise stated and all concentrations are on a wt/wt basis.

Example 1

[0035] Bright mild steel 1 inch x 1 inch (25.4 x 25.4 mm) coupons having an average weight of 7.5g were thoroughly

washed with acetone followed by ethanol and stored in kerosene until required. Immediately prior to use, the coupons were washed with acetone.

[0036] Test coupons prepared as described previously were immersed for about two minutes in a 1% w/w solution, in a water insoluble poly(oxyalkylene) glycol having a viscosity of 460 cSt at 40°C and available from Imperial Chemical Industries PLC as EMKAROX VG 462 lubricant base, of a 1:3 by weight mixture of 2-hydroxy-5-nonylbenzaloxime with a long chain carboxylic acid anhydride. After immersion in the poly(oxyalkylene) glycol solution the steel coupons were subjected to a warm humid atmosphere (90% relative humidity at 40°C). The coupons were inspected at regular intervals for evidence of the first onset of rust. For comparison steel coupons which had been subjected only to cleaning or which had been cleaned and immersed in the poly(oxyalkylene) glycol containing no additive, were also subjected to the warm humid atmosphere. The results are set out in Table One.

Table One

Example or Comp. Ex.	Additive (a)	Time to Rust (days)
1	1BAO + 3ASA	21
A	NIL	4
B	UT	1

Notes to Table One

[0037]

- (a) BAO is 2-hydroxy-5-nonylbenzaloxime
 ASA is a 2:1 by weight mixture of 2-dodecenylsuccinic anhydride and 2-tetradecenylsuccinic anhydride.
 NIL means the test coupons were immersed in the poly(oxyalkylene) glycol which contained no additive.
 UT means that the test coupons were clean but had not been subjected to further treatment.

Example 2

[0038] Test coupons cleaned as described in Example 1 were immersed, for two minutes, in a 1% w/w solution of an additive, in a water insoluble poly(oxyalkylene) glycol having a viscosity of 221 cSt at 40°C and available from Imperial Chemical Industries PLC as 'EMKAROX' VG222 lubricant base.

[0039] The treated test coupons were transferred to distilled water maintained at 50°C. The coupons were inspected at regular intervals for evidence of rust. The results are set out in Table Two.

Table Two

Example or Comp. Ex.	Additive (a) (b)	Time to Rust (days)
C	AFA	0.5
2	1BAO + 3ASA	72
D	NIL	0.5

Notes to Table Two

[0040]

- (a) is as defined in Notes to Table One.
 (b) AFA is a commercially available alkanolamine salt of a fatty acid.

Example 3

[0041] The procedure of ASTM Test Method D 665A was carried out using a 0.5% w/w solution of the mixture used in Example 1 in a water soluble poly(oxyalkylene) glycol having a viscosity of 131 cSt at 40°C and available from Imperial Chemical Industries PLC as 'EMKAROX' VG 132W lubricant base.

[0042] Pass or Fail was assessed in accordance with the test method. The results are set out in Table Three.

Table Three

Example or Comp. Ex.	Additive (a)	Result
3	1BAO + 3 ASA	Pass
E	NIL	Fail

Notes to Table Three

[0043]

(a) is as defined in Notes to Table One.

Examples 4 and 5

[0044] The procedure of ASTM Test Method D 665B was carried out using a 3% w/w aqueous solution of sodium chloride and either a 0.25% w/w or a 1% w/w solution of an additive or additive mixture in the poly(oxyalkylene) glycol used in Example 2.

[0045] The metal specimens were weighed prior to and at the end of the test in order to determine weight loss. Pass or Fail was also assessed in accordance with the test method. The results are set out in Table Four.

Table Four

Example or Comp Ex	Additive		Wt loss (mg)	Pass or Fail
	Type (a)	Amount (%)		
4	1BAO+3ASA	1	0.2	Pass
L	ASA	1	0.4	Pass
F	BAO	1	20.7	Fail
G	NIL	0	25.0	Fail
5	1BAO+3ASA	0.25	0.7	Fail
M	ASA	0.25	1.8	Fail
H	BAO	0.25	24.2	Fail
I	NIL	0	25.0	Fail

Notes to Table Four

[0046]

(a) is as defined in Notes to Table One.

Example 6

[0047] A sample of a 1% w/w solution of an additive mixture in the poly(oxyalkylene) glycol used in Example 2 was placed in a beaker, weighed and then held in a forced draught oven at 180°C.

[0048] The beaker was removed at various time intervals, allowed to cool to room temperature, weighed and returned to the oven. Percentage weight losses were determined at three time intervals, and the results set out in Table Five.

[0049] These results indicate the enhanced anti-oxidation properties of the composition of the invention.

Table Five

Example or Comp.Ex.	Additive (a)	Time (hours)		
		24	48	66
J	Nil	44	79	88
6	IBAO + 3ASA	35	62	76

Notes to Table Five**[0050]**

(a) is defined in Notes to Table One.

Example 7

[0051] Using a Mettler TA 4000 Differential Scanning Calorimeter, runs were carried out using a 1% w/w solution of an additive mixture in the poly(oxyalkylene)glycol used in Example 2.

[0052] The sample was weighed onto a small aluminium pan with a perforated lid and the temperature raised from 25 to 350°C at 10°C/minute with an airflow rate of 80 ml/min. A plot was obtained depicting the relationship between any heat flow generated and the increasing temperature experienced by the sample.

[0053] The onset temperature of the exotherm was recorded and the results are set out in Table Six. The results illustrate an improvement in anti-oxidation.

Table Six

Example or Comp. Ex.	Additive (a)	Wt. of sample (mg)	Onset temperature of exotherm (°C)
7	IBAO + 3ASA	4.71	163
K	Nil	4.48	153

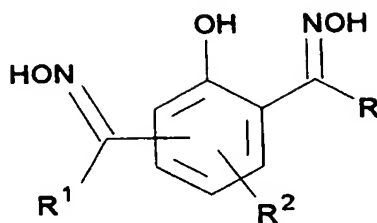
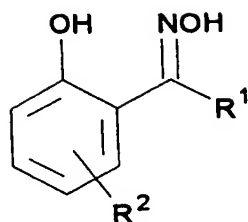
Notes to Table Six**[0054]**

(a) is defined in Notes to Table One.

Claims

1. A composition comprising

- a) a liquid poly(oxyalkylene) glycol derivative,
- b) a carboxylic acid anhydride having a long saturated or unsaturated hydrocarbon chain which contains at least 6 carbon atoms, and
- c) a hydroxyoxime of the general formula:



or

where

R1 is a hydrogen atom or a substituted or unsubstituted hydrocarbon group; and

R2 is a substituted or unsubstituted hydrocarbon group in which the hydrocarbon group contains from 5 to 22 carbon atoms.

2. A composition as claimed in claim 1 wherein the liquid poly(oxyalkylene) glycol derivative has a viscosity measured at 40°C using the procedure of ASTM Test Method D445 which is in the range of from 5 to 500,000 cSt (5×10^{-6} to $5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$).

3. A composition as claimed in claim 2 wherein

i the liquid poly(oxyalkylene) glycol derivative is a water insoluble material based solely or predominantly on oxyalkylene repeat units and which has a viscosity measured at 40°C using the procedure of ASTM Test Method D445 which is in the range of from 10 to 1200 cSt (10^{-5} to $1.2 \times 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$); and

ii the hydroxyoxime is a mono-oxime which is a 2-hydroxy-5-alkylbenzaloxime or a 2-hydroxy-5-alkylbenzoxetoxime.

4. A composition as claimed in claim 2 wherein

i the liquid poly(oxyalkylene) glycol derivative is a water soluble material based solely or predominantly on oxyalkylene repeat units and which has a viscosity measured at 40°C using the procedure of ASTM Test Method D445 which is in the range of from 25 to 250,000 cSt (2.5×10^{-5} to $2.5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$); and

ii the hydroxyoxime is a mono-oxime which is a 2-hydroxy-5-alkylbenzaloxime or a 2-hydroxy-5-alkylbenzoxetoxime.

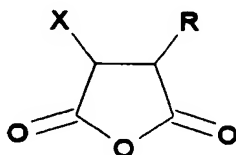
5. A composition as claimed in any one of claims 1 to 4 wherein the composition includes a fatty acid corresponding to the anhydride.

6. A composition as claimed in any one of claims 1 to 5 wherein

i the carboxylic acid anhydride is an anhydride of an α, β -dicarboxylic acid; and

ii the hydroxyoxime is a mono-oxime which is a 2-hydroxy-5-nonylbenzaloxime or a 2-hydroxy-5-nonylacetophenone oxime.

7. A composition as claimed in any one of claims 1 to 6 wherein the acid anhydride is of the general formula (I):



where

R is a linear or branched, saturated or unsaturated hydrocarbyl radical;

X is hydrogen or an alkyl, aryl, alkoxy or aralkyl group, or

R and/or X are linked to another cyclic anhydride group which may be the same or different, or

R and X together form a ring system which is substituted with at least one long chain hydrocarbyl radical; and

the weight ratio of the mixture of the acid anhydride, or a mixture thereof with the corresponding acid, to the hydroxyoxime is between 1:99 and 99:1.

8. A composition as claimed in claim 7 wherein the acid anhydride is one in which X is hydrogen and R nonyl, decyl, decenyl, dodecyl, dodecenyl, tetradecyl, tetradecenyl, octadecyl or octadecenyl.
9. A composition as claimed in claim 7 wherein the acid anhydride is one in which R is an isobutylene polymer made from but-1-ene, but-2-ene or isobutene and having a molecular weight from about 200 to about 8000.
10. A composition as claimed in any one of claims 1 to 9 wherein the composition contains from 0.01% to 30% by weight of the acid anhydride.
11. A composition as claimed in any one of claims 1 to 10 wherein the weight ratio of the mixture of the acid anhydride, or the mixture thereof with the corresponding acid, to the hydroxyoxime is from 1:10 and 10:1.
12. A composition as claimed in claim 11 wherein the weight ratio of the mixture of the acid anhydride, or the mixture thereof with the corresponding acid, to the hydroxyoxime is from 1:5 and 5:1.
13. A method of treating a metal surface which comprises contacting a the metal surface with a composition as claimed in any one of claims 1 to 12.
14. The use of compositions as claimed in any one of claims 1 to 12 as treatments for improving the resistance of a metal to oxidative and/or other deterioration.

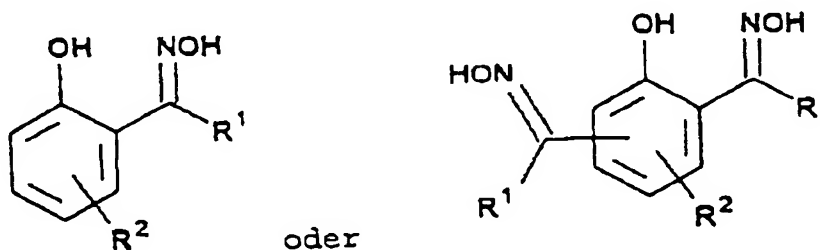
Patentansprüche

1. Zusammensetzung, die umfasst

a) ein flüssiges Poly(oxyalkylen)glykolderivat,

b) ein Carbonsäureanhydrid mit einer langen gesättigten oder ungesättigten Kohlenwasserstoffkette, die wenigstens 6 Kohlenstoffatome aufweist, und

c) ein Hydroxyoxim der allgemeinen Formel:



worin

R1 ein Wasserstoffatom oder eine substituierte oder nichtsubstituierte Kohlenwasserstoffgruppe ist; und

R2 eine substituierte oder nichtsubstituierte Kohlenwasserstoffgruppe ist, bei der die Kohlenwasserstoffgruppe 5 bis 22 Kohlenstoffatome enthält.

2. Zusammensetzung nach Anspruch 1, bei der das flüssige Poly(oxyalkylen)glykolderivat eine Viskosität aufweist, die, gemessen bei 40°C unter Verwendung des Verfahrens der ASTM-Testmethode D445, im Bereich von 5 bis 500.000 cSt (5×10^{-6} bis $5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$) liegt.

3. Zusammensetzung nach Anspruch 2, bei der

i das flüssige Poly(oxyalkylen)glykolderivat ein wasserunlösliches Material ist, das ausschließlich oder überwiegend auf sich wiederholenden Oxyalkylen-Einheiten basiert und das eine Viskosität aufweist, die, gemessen bei 40°C unter Verwendung des Verfahrens der ASTM-Testmethode D445, im Bereich von 10 bis 1200 cSt (10^{-5} bis $1,2 \times 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$) liegt; und

ii das Hydroxyoxim ein Monooxim ist, welches ein 2-Hydroxy-5-alkylbenzaläoxim oder ein 2-Hydroxy-5-alkylbenzoketoxim ist.

4. Zusammensetzung nach Anspruch 2, bei der

i das flüssige Poly(oxyalkylen)glykolderivat ein wasserlösliches Material ist, das ausschließlich oder überwiegend auf sich wiederholenden Oxyalkylen-Einheiten basiert, und das eine Viskosität aufweist, die, gemessen bei 40°C unter Verwendung des Verfahrens der ASTM-Testmethode D445, im Bereich von 25 bis 250.000 cSt ($2,5 \times 10^{-5}$ bis $2,5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$) liegt; und

ii das Hydroxyoxim ein Monooxim ist, das ein 2-Hydroxy-5-alkylbenzaldoxim oder ein 2-Hydroxy-5-alkylbenzoketoxim ist.

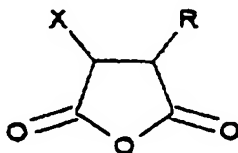
5. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 4, wobei die Zusammensetzung eine zu dem Anhydrid korrespondierende Fettsäure enthält.

6. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 5, bei der

i das Carbonsäureanhydrid ein Anhydrid einer α, β -Dicarbonsäure ist; und

ii das Hydroxyoxim ein Monooxim ist, das ein 2-Hydroxy-5-nonylbenzaldoxim oder ein 2-Hydroxy-5-nonylacetophenonoxim ist.

7. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 6, bei der das Säureanhydrid die allgemeine Formel (I) aufweist:



worin

R ein linearer oder verzweigter, gesättigter oder ungesättigter Kohlenwasserstoffrest ist;

X Wasserstoff oder eine Alkyl-, Aryl-, Alkoxy- oder Aralkylgruppe ist, oder

R und/oder X mit einer anderen cyclischen Anhydridgruppe verbunden sind, die die gleiche ist oder unterschiedlich sein kann, oder

R und X zusammen ein Ringsystem bilden, welches mit wenigstens einem Kohlenwasserstoffrest mit langer

Kette substituiert ist; und

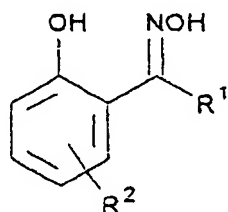
das Gewichtsverhältnis der Mischung des Säureanhydrids, oder einer Mischung davon mit der korrespondierenden Säure, zu dem Hydroxyoxim zwischen 1:99 und 99:1 liegt.

8. Zusammensetzung nach Anspruch 7, bei der das Säureanhydrid eines ist, bei dem X Wasserstoff ist und R Nonyl, Decyl, Decenyl, Dodecyl, Dodecenyl, Tetradecyl, Tetradecenyl, Octadecyl oder Octadecenyl.
9. Zusammensetzung nach Anspruch 7, bei der das Säureanhydrid eines ist, bei dem R ein ~~tertiäres~~ **tertiäres** Polymer ist, das aus But-1-en, But-2-en oder Isobuten hergestellt ist und ein Molekulargewicht von etwa 200 bis etwa 8000 aufweist.
10. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 9, wobei die Zusammensetzung 0,01 bis 30 Gew.-% des Säureanhydrids enthält.
11. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 10, bei der das Gewichtsverhältnis der Mischung des Säureanhydrids, oder der Mischung davon mit der korrespondierenden Säure, zu dem Hydroxyoxim zwischen 1:10 und 10:1 beträgt.
12. Zusammensetzung nach Anspruch 11, bei der das Gewichtsverhältnis der Mischung des Säureanhydrids, oder der Mischung davon mit der korrespondierenden Säure zu dem Hydroxyoxim zwischen 1:5 und 5:1 beträgt.
13. Verfahren zum Behandeln einer Metalloberfläche, das das Kontaktieren der Metalloberfläche mit einer Zusammensetzung nach irgendeinem der Ansprüche 1 bis 12 umfasst.
14. Verwendung der Zusammensetzungen nach irgendeinem der Ansprüche 1 bis 12 als Behandlungsmittel, um die Beständigkeit eines Metalls gegenüber oxidativer und/oder anderer Zerstörung zu verbessern.

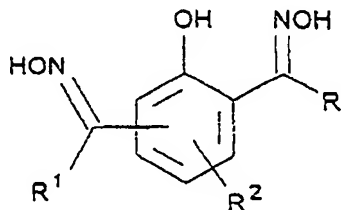
Revendications

1. Composition comprenant :

- (a) un dérivé poly(oxyalkylène)glycol liquide
- (b) un anhydride d'acide carboxylique ayant une longue chaîne hydrocarbonée saturée ou non saturée qui contient au moins 6 atomes de carbone, et
- (c) un hydroxyoxime de formule générale :



ou



dans laquelle

- R¹ représente un atome d'hydrogène ou un groupe hydrocarboné substitué ou non substitué ; et
 - R² représente un groupe hydrocarboné substitué ou non substitué dans lequel le groupe hydrocarboné contient 5 à 22 atomes de carbone.
2. Composition selon la revendication 1, dans laquelle le dérivé poly(oxyalkylène)glycol liquide a une viscosité, mesurée à 40°C selon la procédure de la technique de test ASTM D445, qui est comprise entre 5 et 500.000 cSt (5×10^6 à $5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$).
 3. Composition selon la revendication 2, dans laquelle

(i) le dérivé poly(oxyalkylène)glycol liquide est un matériau hydrosoluble à base uniquement ou de façon prédominante, d'unités répétitives oxyalkylène et d'une viscosité, mesurée à 40°C selon la procédure de la technique de test ASTM D445, qui est comprise entre 10 et 1200 cSt (10^{-5} à $1,2 \times 10^{-3} \text{ m}^2 \cdot \text{s}^{-1}$) ; et

(ii) l'hydroxyoxime est un mono-oxime qui est un 2-hydroxy-5-alkylbenzaldoxime ou un 2-hydroxy-5-alkylbenzocétoxime.

4. Composition selon la revendication 2, dans laquelle

(i) le dérivé poly(oxyalkylène)glycol liquide est un matériau hydrosoluble à base uniquement ou de façon prédominante, d'unités répétitives oxyalkylène et d'une viscosité, mesurée à 40°C selon la procédure de la technique de test ASTM D445, qui est comprise entre 25 et 250.000 cSt ($2,5 \times 10^6$ à $2,5 \times 10^{-1} \text{ m}^2 \cdot \text{s}^{-1}$) ; et

(ii) l'hydroxyoxime est un mono-oxime qui est un 2-hydroxy-5-alkylbenzaldoxime ou un 2-hydroxy-5-alkylbenzocétoxime.

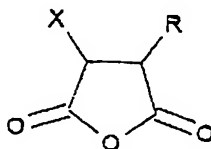
5. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle ladite composition comprend un acide gras correspondant à l'anhydride.

6. Composition selon l'une quelconque des revendications 1 à 5, dans laquelle :

(i) l'anhydride d'acide carboxylique est un anhydride d'un acide α, β -dicarboxylique ; et

(ii) l'hydroxyoxime est un mono-oxime qui est un 2-hydroxy-5-nonylbenzaldoxime ou un 2-hydroxy-5-nonylbenzophénone oxime.

7. Composition selon l'une quelconque des revendications 1 à 6, dans laquelle l'anhydride d'acide est de formule générale (I) :



dans laquelle :

- R représente un radical hydrocarbyle linéaire ou ramifié, saturé ou non saturé ;
- H représente l'hydrogène ou un groupe alkyle, aryle, alcoxy ou aralkyle ou bien
- R et/ou X sont reliés à un autre groupe anhydride cyclique qui peut être le même ou être différent, ou bien
- R et X forment ensemble un système cyclique qui est substitué par au moins un radical hydrocarbyle à longue chaîne ; et

le rapport pondéral entre le mélange de l'anhydride d'acide ou un mélange de celui-ci avec l'acide correspondant, et l'hydroxyoxime est compris entre 1/99 et 99/1.

8. Composition selon la revendication 7, dans laquelle l'anhydride d'acide est un anhydride dans lequel X est l'hydrogène et R représente un groupe nonyle, décyle, décényle, dodécyle, dodécényle, tétradécyle, tétradécényle, octadécyle ou octadécényle.

9. Composition selon la revendication 7, dans laquelle l'anhydride d'acide est un anhydride dans lequel R est un polymère isobutylène fait à partir de but-1-ène, de but-2-ène ou d'isobutène et qui a un poids moléculaire d'environ 200 à environ 8000.

10. Composition selon l'une quelconque des revendications 1 à 9, dans laquelle ladite composition contient 0,01 % à 30 % en poids, de l'anhydride d'acide.

11. Composition selon l'une quelconque des revendications 1 à 10, dans laquelle le rapport pondéral entre le mélange de l'anhydride d'acide ou le mélange de celui-ci avec l'acide correspondant, et l'hydroxyoxime est compris entre 1/10 et 10/1.

12. Composition selon la revendication 11, dans laquelle le rapport pondéral entre le mélange de l'anhydride d'acide ou le mélange de celui-ci avec l'acide correspondant, et l'hydroxyoxime est compris entre 1/5 et 5/1.
13. Procédure de traitement d'une surface métallique qui comprend la mise en contact de la surface métallique avec une composition selon l'une quelconque des revendications 1 à 12.
14. Utilisation de compositions selon l'une quelconque des revendications 1 à 12 en tant que traitements destinés à améliorer la résistance d'un métal à une détérioration oxydante et/ou autre.